

Raman spectra shows good agreement, especially with the results of Kohlrausch and Stockmair. The superior resolving power of the prism spectrometer used in this work is illustrated by comparison with the work of Gordy⁷ on dioxane-water mixtures using a fluorite prism spectrometer. In the region 5.9 to $6.5\ \mu$ (1695 to $1538\ \text{cm.}^{-1}$) Gordy used too thin a cell ($0.02\ \text{mm.}$) to detect the six weak bands found by us. In the region from 4.4 to $5.2\ \mu$ (2273 to $1923\ \text{cm.}^{-1}$) Gordy finds one band at $5.05\ \mu$ ($1980\ \text{cm.}^{-1}$). Our instrument resolves this band into two at 1964 and $1982\ \text{cm.}^{-1}$. The single band found by Gordy at $3.38\ \mu$ ($2959\ \text{cm.}^{-1}$) was resolved by our prism instrument into three bands as shown in the curve inserted in Fig. 1 (top). Subsequent examination on the grating spectrometer showed four bands at 2855 , 2891 , 2917 and $2961\ \text{cm.}^{-1}$ (Fig. 1, bottom).

(7) Gordy, *J. Chem. Phys.*, **4**, 769 (1936).

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Summary

The infrared absorption of liquid and gaseous 1,4-dioxane has been investigated between 1.4 and $14.0\ \mu$ using a rock salt spectrometer of unusually high resolving power. The region from 2.27 to $3.72\ \mu$ has also been investigated using a prism-grating spectrometer. The absorption in the gas is not much different than that observed in the liquid. In passing from the liquid to the gas there is a slight shift to higher frequencies: For example, the liquid bands in the $3.45\ \mu$ region are shifted 4 to 9 wave numbers, and the vapor band shape is characteristic of the envelope of vibration-rotation lines.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions of Electrolytes as a Function of the Concentration. V. Sodium Chloride

BY GRINNELL JONES AND SCHUYLER M. CHRISTIAN

This paper gives data on the viscosity of aqueous solutions of sodium chloride at both 25 and 0° from 0.002 up to $2\ N$. The earlier papers¹ of this series should be consulted for a discussion of the historical background and theoretical interest of the problem.

The best measurements at 25° appear to be those of Ruby Kawai;² at 18° those of Grüneisen;³ and at 0° those of Lyle and Hosking.⁴ The only measurements at extreme dilution known to us are those of Bousfield⁵ at 18° which extend down to $0.0017\ N$.

The best sodium chloride available by purchase was dissolved, filtered through a sintered glass filter, then precipitated in a silica dish by passing hydrochloric acid gas into the solution

and dried in a centrifuge. The process, except the filtration, was then repeated and the salt finally dried by ignition to a red heat in a platinum dish. The solutions were made up by weight and the period of flow determined in an Ostwald viscometer, the same instrument used by Jones and Stauffer. The timing was done by the automatic photoelectric cell method developed by Jones and Talley. The results are shown in Tables I and II. The figures for the density are the averages of two or three independent determinations which rarely differed by more than 0.001% , obtained with different pycnometers of approximately 60-ml. capacity.

Unfortunately the density determinations on the $2\ N$ solutions were omitted through an oversight, but this figure has been estimated with sufficient precision for the purpose from the data of Baxter and Wallace.⁶ The fourth column gives the values of $d_{t,c}/d_{0,t_0}$, which is the average of results obtained with at least two fillings of the viscometer and of several runs on each filling.

(1) Grinnell Jones and M. Dole, *THIS JOURNAL*, **51**, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933); *Physics*, **4**, 215 (1933); Grinnell Jones and H. J. Fornwalt, *THIS JOURNAL*, **57**, 2041 (1933); **58**, 619 (1936); Grinnell Jones and R. E. Stauffer, *ibid.*, **58**, 2558 (1936).

(2) C. E. Ruby and J. Kawai, *ibid.*, **48**, 1119 (1926).

(3) E. Grüneisen, *Wiss. Abhandl. physik.-tech. Reichsanstalt*, **4**, 245 (1905).

(4) T. R. Lyle and R. Hosking, *Phil. Mag.*, **3**, 487 (1902).

(5) W. R. Bousfield, *Phil. Trans.*, **206A**, 101 (1906).

(6) G. P. Baxter and C. C. Wallace, *THIS JOURNAL*, **38**, 83 (1916).

TABLE I
DENSITY AND RELATIVE VISCOSITY OF SODIUM CHLORIDE SOLUTIONS IN WATER AT 25°

Concn., <i>c</i>	Density d_{25}^4	$\frac{d\rho c}{d\rho_0}$	Relative viscosity	$\frac{\eta - 1}{c}$	Jones and Dole equations Simple $\Delta\phi \times 10^5$	Extended $\Delta\phi \times 10^5$
0.002	0.99716	1.00043	1.00043	0.21	0	0
.005	.99728	1.00080	1.00081	.16	+ 2	+ 1
.010	.99749	1.00145	1.00146	.146	- 5	- 7
.02	.99790	1.00257	1.00259	.130	- 12	-16
.05	.99913	1.00540	1.00544	.108	- 7	-15
.1	1.00121	1.00988	1.00995	.099	+ 2	-13
.2	1.00528	1.01861	1.01874	.0937	+ 19	- 2
.5	1.01735	1.04570	1.04603	.0921	+ 7	+ 1
1.0	1.03708	1.09511	1.09582	.0958	- 208	+ 4
2.0021 (2.0)	(1.07527)	1.21716	1.21886 (1.2186)	.1094	-1238	- 1

Root equation $d_{25}^4 = 0.997074 + 0.041882 c - 0.001878 c^{3/2}$

Range of validity, <i>N</i>	Average deviation, %
1	0.0004

Jones and Dole equations

$\eta = 1 + 0.00670\sqrt{c} + 0.07866 c$	0.2	.003
$\eta = 1 + 0.00670\sqrt{c} + 0.07620 c + 0.01291 c^2$	1.0	.005
$\phi = 1 - 0.00618\sqrt{c} - 0.07913 c$	0.5	.005
$\phi = 1 - 0.00618\sqrt{c} - 0.07729 c - 0.004005 c^2$	2.0	.007

TABLE II
DENSITY AND RELATIVE VISCOSITY OF SODIUM CHLORIDE SOLUTIONS AT 0°

Concn., <i>c</i>	Density d_{25}^4	$\frac{d\rho c}{d\rho_0}$	Relative viscosity	$\frac{\eta - 1}{c}$	Jones and Dole equations Simple $\Delta\phi \times 10^5$	Extended $\Delta\phi \times 10^5$
0.002	0.99996	1.00037	1.00037	0.18	- 12	-12
.005	1.00010	1.00037	1.00037	.073	+ 7	+ 7
.01	1.00032	1.00072	1.00072	.072	- 2	- 4
.02	1.00078	1.00126	1.00126	.063	- 13	-16
.05	1.00211	1.00211	1.00211	.042	+ 11	+ 8
.1	1.00438	1.00382	1.00382	.038	+ 3	-35
.2	1.00877	1.00692	1.00691	.0345	- 3	+40
.5022 (.5)	1.02194	1.01907	1.01906 (1.01895)	.0380	- 343	+51
1.00588 (1.0)	1.04308	1.04898	1.04900 (1.04858)	.0487	-1803	-53
2.01766 (2.0)	(1.08362)	1.14730	1.14750 (1.14534)	.0731	-7372	+10

Root equation $d_0^4 = 0.99987 + 0.04605 c - 0.00307 c^{3/2}$

Range of validity, <i>N</i>	Average deviation, %
1	0.001

Jones and Dole equations

$\eta = 1 + 0.00448\sqrt{c} + 0.02438 c$	0.2	.008
$\eta = 1 + 0.00448\sqrt{c} + 0.018923 c + 0.025284 c^2$	2	.011
$\phi = 1 - 0.00456\sqrt{c} - 0.02397 c$.2	.008
$\phi = 1 - 0.00456\sqrt{c} - 0.02228 c - 0.01897 c^2$	2	.023

The relative viscosity, η , given in Column 4 is obtained from these figures by the application of a small kinetic energy correction.

In a few cases a correction of 0.001 or 0.002% has been applied to the data as given to bring them to the round concentration given in the first column. For the 2 *N* solution at 25° and for the three strongest solutions at 0° this cor-

rection is so large that it seemed best to publish the data as actually determined. The corrected figures at the round concentration are given in parentheses.

Interpretation of the Data

The experimental data given above on the density of sodium chloride up to 1 *N* may be

expressed with an average deviation of only 0.001% by the equations having the form suggested by Root.⁷

$$d^{25}_4 = 0.997074 + 0.041882c - 0.001878c^{3/2}$$

$$d^0_4 = 0.99987 + 0.04605c - 0.00307c^{3/2}$$

The fifth column shows that the "Grüneisen Effect" is shown by sodium chloride although it is not so pronounced as has been observed with salts of a higher valence type.

The results for the viscosity at 25° can be expressed by the equation $\eta = 1 + 0.00670\sqrt{c} + 0.07866c$ up to 0.2 *N* with an average deviation of only 0.003%. By adding a term proportional to the square of the concentration the equation which is shown at the bottom of Table I may be obtained which fits the data with an average deviation of 0.005% up to 1 *N*. If the results are expressed in terms of fluidity, ϕ , instead of viscosity there is a slight improvement in that the simple two-parameter equation holds up to 0.5 *N* and the extended three-parameter equation holds up to 2 *N*.

At 0° we find that as usual the relative viscosity is less than at 25°. Here there is little

(7) W. C. Root, *THIS JOURNAL*, **55**, 850 (1933).

to choose between the equations expressed in terms of viscosity or of fluidity. The average deviations are slightly greater than at 25°, probably because of the greater difficulty in maintaining temperature control during the hot summer weather when this work was done.

The coefficient of the square root term (*A*) computed by the Falkenhagen and Vernon⁸ equation is 0.0060 at 25° and 0.0056 at 0°, whereas the experimentally determined values are 0.0067 and 0.0045, respectively. The agreement is not quite as good as has been found in several other cases, especially at 0°.

Summary

1. The absolute density and relative viscosity of many aqueous solutions of sodium chloride have been determined at 0 and 25°, covering the range of concentration from 0.002 to 2 *N*.

2. The density of these solutions as a function of the concentration can be expressed by the Root equation, and the viscosity by the Jones and Dole equation.

(8) H. Falkenhagen and E. L. Vernon, *Physik. Z.*, **33**, 140 (1932).

CAMBRIDGE, MASS.

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The Heat Capacities of Molybdenite and Pyrite at Low Temperatures¹

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In previous papers³ the writer has presented low temperature thermal data on manganese sulfide, ferrous sulfide, calcium sulfide and the sulfides of copper and lead. The present paper deals with the heat capacities of molybdenite and pyrite.

The methods, apparatus and accuracy have been described previously.⁴

Materials

Both samples used in this investigation were naturally occurring minerals. The pyrite used was taken from one large specimen. It was broken, and samples that did not show particles of quartz or discoloration were selected. The material was then crushed and screened, the

finer being discarded. Analysis of the sample for iron content indicated a purity of 99.24% FeS₂. The only detectable impurity was 0.02% SiO₂. A 301.4-g. sample with a density of 4.951 at 22.4° was studied.

The sample of molybdenite consisted of laminated flakes about 5 mm. in diameter. Since they could not be crushed, the sample was put through a food chopper and screened to size. The only impurities found in the sample were 0.31% FeS₂ and 0.53% SiO₂, which were corrected for in the specific heat measurements. The calorimeter was filled with 166.4 g., with a density of 4.991 at 20.0°.

The Specific Heats

Specific heat measurements have been made on pyrite from 21.7 to 84°K. by Eucken and Schwerts,⁵ and three points have been measured by

(5) Eucken and Schwerts, *Ber. deut. physik. Ges.*, **15**, 582 (1913).

(1) Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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(3) Anderson, *THIS JOURNAL*, **53**, 476 (1931); **54**, 107 (1932).

(4) Anderson, *ibid.*, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).